

EEDP-01-8  
March 1987



# *Environmental Effects of Dredging Technical Notes*

## SIMPLIFIED APPROACH FOR EVALUATING BIOAVAILABILITY OF NEUTRAL ORGANIC CHEMICALS IN SEDIMENT

**PURPOSE:** This note outlines a tiered approach for evaluation of bioavailability of neutral organic contaminants in sediment and provides a method for the numerical expression of bioavailability. The first tier is a simple mathematical calculation, from sediment chemistry, of maximum potential bioaccumulation. If Tier I calculations indicate potential bioaccumulation of neutral organic contaminants to concentrations of concern, then Tier II laboratory tests could be conducted to determine the actual amount of bioaccumulation. In the second tier, bioaccumulation is assessed in laboratory exposures of organisms to the contaminated sediment. Comparison of the actual bioaccumulation at projected steady state to the calculated maximum potential bioaccumulation results in a measure of bioavailability.

**BACKGROUND:** Public laws regulating dredged material disposal (Section 404 of the Clean Water Act and Section 103 of the Ocean Dumping Act) require ecological evaluation prior to the permitting of operations. Assessment of the potential for bioaccumulation of chemical contaminants in sediment is required as part of the evaluation process. Current methodology (USEPA/CE 1977) involves exposure of aquatic organisms for a period of 10 days to sediment deposited in aquaria. Analysis of tissues of surviving organisms at the end of the exposure period indicates whether detectable bioaccumulation occurred and thus whether the sediment contains specific chemicals of concern in bioavailable forms. The approach is applied empirically on a case-by-case basis and is limited to simple demonstration of uptake. The procedure yields no information concerning concentrations that would actually be accumulated by organisms given prolonged exposure to contaminated sediment, i.e., the projected achievable bioaccumulation. Nor is there any means of using analyses of chemical contaminants in sediment to estimate the concentrations that could theoretically occur in exposed organisms, i.e., the potential for bioaccumulation.

Sediment evaluations that are more effective and informative than the simple 10-day bioaccumulation test can be accomplished using a tiered approach. In the tiered approach, the potential for bioaccumulation is estimated; if estimates of potential bioaccumulation are high enough to be of concern, then the projected achievable bioaccumulation at steady state is determined. This two-tiered method for evaluating organic chemical contaminants in sediment was proposed by McFarland (1984) and McFarland and Clarke (1986).

Tier I evaluation uses results of sediment chemical analysis to estimate theoretical maximum tissue residues that would occur in an exposed organism if

DISTRIBUTION STATEMENT A  
Approved for public release  
Distribution Unlimited

19950327 140

all of a chemical of interest in the sediment were bioavailable. Tier II evaluation follows if the maxima calculated in Tier I are judged unacceptable by applicable criteria, levels of concern, or action levels. Tier II involves exposures of aquatic biota to sediment with time-sequenced sampling over a sufficient exposure period (e.g., on days 2, 4, 10, 17, and 30) to allow for projection of steady-state tissue residues using a kinetic model. Tier I calculations represent the maximum bioaccumulation that could occur from a given sediment. Tier II steady-state tissue residues represent the maximum bioaccumulation that is likely to occur in the field (i.e., projected achievable) under exposure conditions similar to those used in the laboratory. Comparison of potential bioaccumulation from Tier I with projected achievable bioaccumulation in Tier II results in a quantitative estimation of bioavailability of chemicals in the sediment under investigation.

This note briefly describes the two-tiered approach and presents an example using laboratory exposures of an aquatic organism to a harbor sediment contaminated with polychlorinated biphenyls (PCBs). More information on the theoretical background and derivation of the approach is found in McFarland (1984) and McFarland and Clarke (1986).

ADDITIONAL INFORMATION OR QUESTIONS: Contact the authors, Mr. Victor McFarland (601) 634-3721 (FTS 542-3721), or Ms. Joan Clarke (601) 634-2954 (FTS 542-2954), or the manager of the Environmental Effects of Dredging Programs, Dr. Robert M. Engler (601) 634-3624 (FTS 542-3624).

### Tier I Evaluation

In the first tier evaluation, knowledge of the distribution of a chemical between sediment and organism is required. Neutral organic chemicals such as PCBs are distributed primarily in the lipids of organisms (Konemann and van Leeuwen 1980, Geyer et al. 1982, Mackay 1982) and in the organic carbon fraction of sediment (Karickhoff 1981). Based on the work of Konemann and van Leeuwen (1980) and Karickhoff (1981), neutral organic chemicals were calculated to have a preference factor of 1.72 for organism lipid over sediment organic carbon. This means that the maximum possible chemical concentration that could result in an organism's lipids would be 1.72 times the concentration of that chemical in the sediment organic carbon. This calculated maximum is called the lipid bioaccumulation potential (LBP):

$$LBP = 1.72(C_s/fOC) \quad (1)$$

where

LBP = equivalent concentration in organism lipid in the same units of concentration as  $C_s$

$C_s$  = concentration of chemical in the sediment (any units of concentration may be used)

fOC = decimal fraction organic carbon content of the sediment

LBP represents a maximum possible contaminant concentration in lipid if the sediment is the only source of that contaminant to the organism.

In practice, sediment would be analyzed for the concentration of a neutral organic chemical of concern and for organic carbon content. LBP would be calculated using Equation 1 and would indicate maximum bioaccumulation potential in the lipid of any organism. It is generally desirable to convert LBP to a whole-body bioaccumulation potential (WBP) for a particular organism of interest. This is done by multiplying LBP by that organism's lipid content (expressed as a decimal fraction of wet weight), as determined by lipid analysis or from reported data:

$$WBP = LBP(fL) \quad (2)$$

where

WBP = maximum whole-body bioaccumulation potential in the same units of concentration as LBP

fL = decimal fraction of an organism's lipid content

If the calculated WBP is acceptable by whatever criteria are applied (e.g., the Food and Drug Administration (FDA) limit of 2 parts per million (ppm) PCB in the edible portions of fish and shellfish), then the sediment evaluation need go no further. If the calculated level is not acceptable (e.g., greater than 2 ppm PCB), then further evaluation could involve biological testing in Tier II.

**Caveats:** Two important assumptions are implicit in these calculations: (1) no metabolic degradation or biotransformation of the chemical and (2) total bioavailability of sediment-associated chemical to the organism. Estimations involving WBP, then, are inherently conservative in that they will present a worst-case prediction of bioaccumulation if sediment is the only source of the contaminant to the organism.

### Tier II Evaluation

In the second tier evaluation, aquatic organisms are exposed to contaminated sediment under constant laboratory conditions for a sufficient period of time for bioaccumulation to occur. If exposure were continued under constant conditions, then a steady state would eventually be achieved in which maximum bioaccumulation would have occurred and the net exchange of the contaminant between sediment and organism would be zero. In practice it is not likely that steady state will be reached in any period of time short enough for

Diet	Special
A-1	

economical laboratory testing. By taking samples sequentially over a short period of constant exposure, a simple kinetic model can be used to project tissue concentrations at steady state (Blau et al. 1975). A computational form of this model integrated for constant exposure is:

$$C_T = \frac{k_1 C_W}{k_2} \left( 1 - e^{-k_2 t} \right) \quad (3)$$

where

$C_T$  = concentration of chemical in organism

$k_1$  = uptake rate constant

$C_W$  = concentration of chemical in exposure medium

$k_2$  = elimination rate constant

$t$  = time

This model can be fitted to time-sequenced exposure data using an iterative nonlinear regression method, such as those in the SAS NLIN procedure (SAS 1985).

As duration of exposure increases, the term  $e^{-k_2 t}$  approaches zero, and

$$C_T = \frac{k_1 C_W}{k_2} = C_{SS} \quad (4)$$

in which  $C_{SS}$  is the whole-body concentration of chemical at steady state.

If steady state is not achieved for a contaminant of interest during the laboratory exposure, then  $C_{SS}$  can be projected using the time-sequenced exposure data in a nonlinear regression procedure, as described above.

The projected achievable  $C_{SS}$  in an organism can then be compared with the potential maximum bioaccumulation WBP estimated from sediment chemistry in Tier I and is expressed as the proportion  $p$  of WBP projected at steady state:

$$p = \frac{C_{SS}}{WBP} \quad (5)$$

If all of the chemical of concern in the sediment to which an organism is exposed were bioavailable, then  $p$  would equal 1. Any value of  $p < 1$  indicates less-than-complete bioavailability of the chemical of concern in a sediment under investigation. The magnitude of  $p$  is a numerical expression of bioavailability that could be of assistance in decisionmaking: for example, in evaluating several disposal alternatives.

Example Using PCB-Contaminated Sediment

Figure 1 presents a flow chart illustrating the steps in the Tier I and Tier II evaluations of contaminated dredged material. Example data from tests of a PCB-contaminated harbor sediment (shown in the following tabulation) demonstrate the calculation of maximum potential bioaccumulation (WBP) and the bioavailability expressed as the proportion  $p$  of WBP actually achieved.

In this example, freshwater mussels were exposed to sediment having four levels of PCB contamination (high, medium, low, and reference) for 30 days at 20° C in a flow-through aquarium system under constant exposure conditions. Tissue samples were taken for chemical residue analysis on days 2, 4, 10, 17,

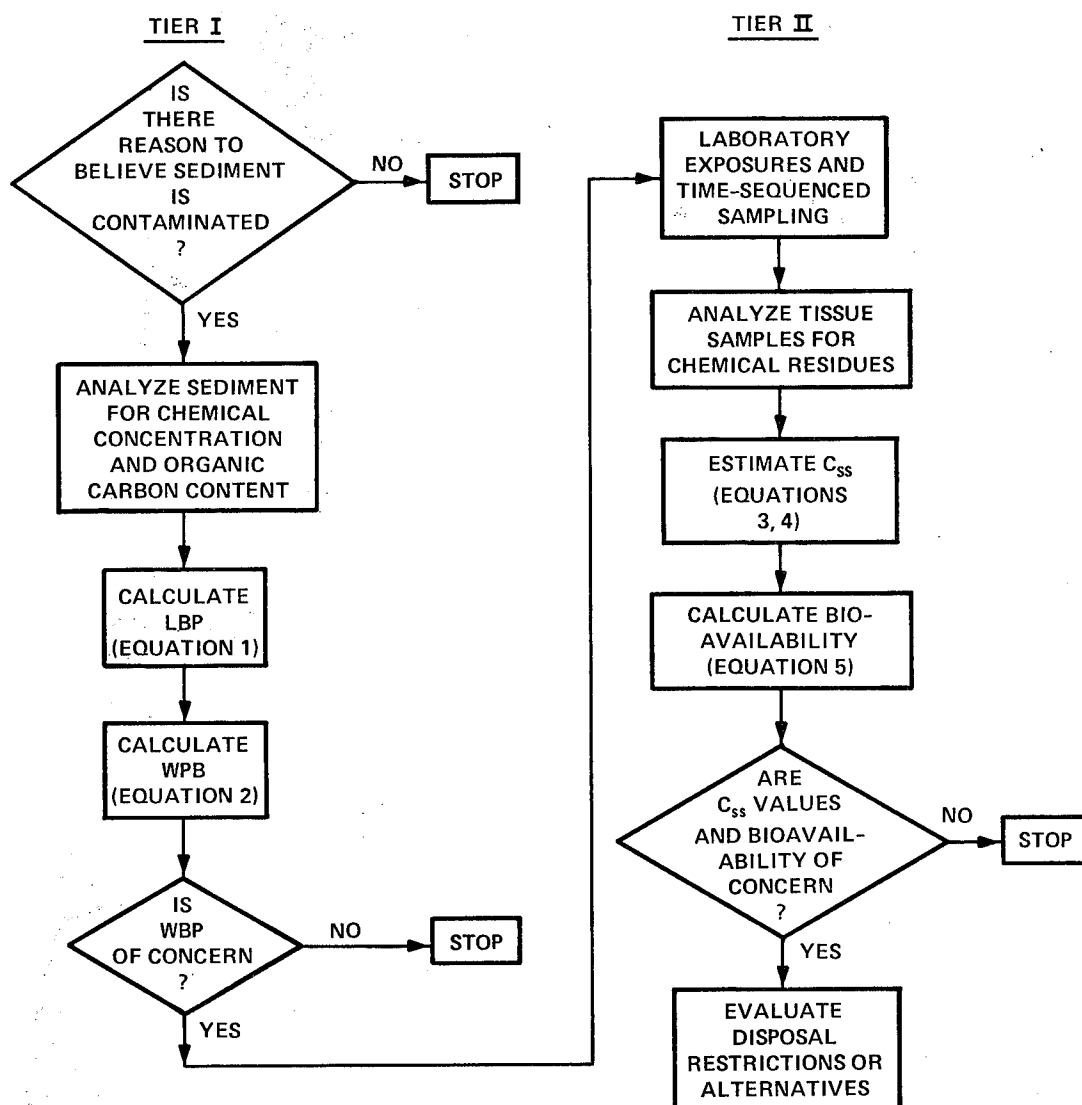


Figure 1. Flow chart for Tier I and Tier II evaluations

a. Tier I evaluation.

Level of Contamination	Sediment			Mussels Lipid Fraction, fL	WBP, ppm (Eq. 2)
	Total PCB $C_s$ , ppm	Organic Carbon fOC	LBP, ppm (Eq. 1)		
High	44	0.016	4730	0.0029	13.7
Medium	33	0.016	3548	0.0031	11.0
Low	4.0	0.016	430	0.0025	1.07
Reference	0.45	0.015	51.6	0.0026	0.13

b. Tier II evaluation.

Level of Sediment Contamination	Total PCB $C_{ss}$ , ppm (Eq. 3, 4)	Bioavailability p (Eq. 5)
High	1.1	0.0802
Medium	0.87	0.0791
Low	0.83	0.7721
Reference	0.054	0.4025

and 30; and the residue data were used to calculate  $C_{ss}$  for total PCB. Details of the experimental design and analysis are described in McFarland and Clarke (1986).

Total PCB concentrations in the sediment ranged from <1 ppm in the reference sediment to 44 ppm in the highly contaminated sediment. LBP values calculated from these concentrations ranged from about 50 to over 4000 ppm. These values represent maximum total PCB concentrations that could occur in the lipids of any aquatic organism exposed to the sediment as the only source of contamination and where that source was totally biologically available. Converting LBP values to a whole-body basis for mussels having a lipid fraction of approximately 0.003 (i.e., 0.3 percent), yielded WBP values that ranged from 0.13 ppm maximum possible bioaccumulation for mussels exposed to the reference sediment to over 13 ppm for mussels exposed to the highly contaminated sediment.

The final step of a Tier I evaluation is a regulatory decision concerning the potential for adverse environmental impact of the sediment analyzed. The regulator might decide, for example, that any sediment having a potential (WBP) for total PCB bioaccumulation greater than the 2-ppm FDA action level would require further evaluation for actual bioaccumulation. Based on the example data for this freshwater sediment, further evaluation (Tier II) would be indicated for the sediment with high and medium levels of contamination, but not for the low contamination or the reference sediment. Tier II calculations using all four sediments are presented in this note for the sake of illustration.

Tier II projected steady-state tissue concentrations  $C_{ss}$  of total PCB ranged from 0.054 ppm for mussels exposed to the reference sediment to 1.1 ppm for mussels exposed to the highly contaminated sediment. These values are clearly much lower than the calculated potential maximum tissue residues (WBP). The regulator might now decide that the PCB content of the sediment under evaluation did not pose a threat to a mussels fishery located near the proposed disposal site under conditions similar to the experiment, since the projected actual PCB bioaccumulation is less than the FDA action level of 2 ppm for edible portions of fish and shellfish.

However, the potential for PCB bioaccumulation in other organisms of greater lipid content exposed to the same sediment might exceed the FDA action level. Using the nomograph shown in Figure 2, it is possible to quickly estimate WBP for organisms of various lipid contents, providing the approximate contaminant concentration  $C_s$  and organic carbon content fOC of the sediment are known. The procedure for using the nomograph is as follows.

- STEP 1. Determine the lipid content of an organism of interest, either from previously reported values or from laboratory analysis, and express the lipid content as percent of whole-body wet weight, rather than as decimal fraction.
- STEP 2. Locate the value on the right-hand vertical axis that corresponds most closely to that lipid content.
- STEP 3. Follow the sloped line until it intersects the sediment concentration  $C_s$ .  $C_s$  may be expressed in any units of concentration and may be selected from any of the four ranges: 0.1-1.0; 1-10; 10-100; or 100-1000.

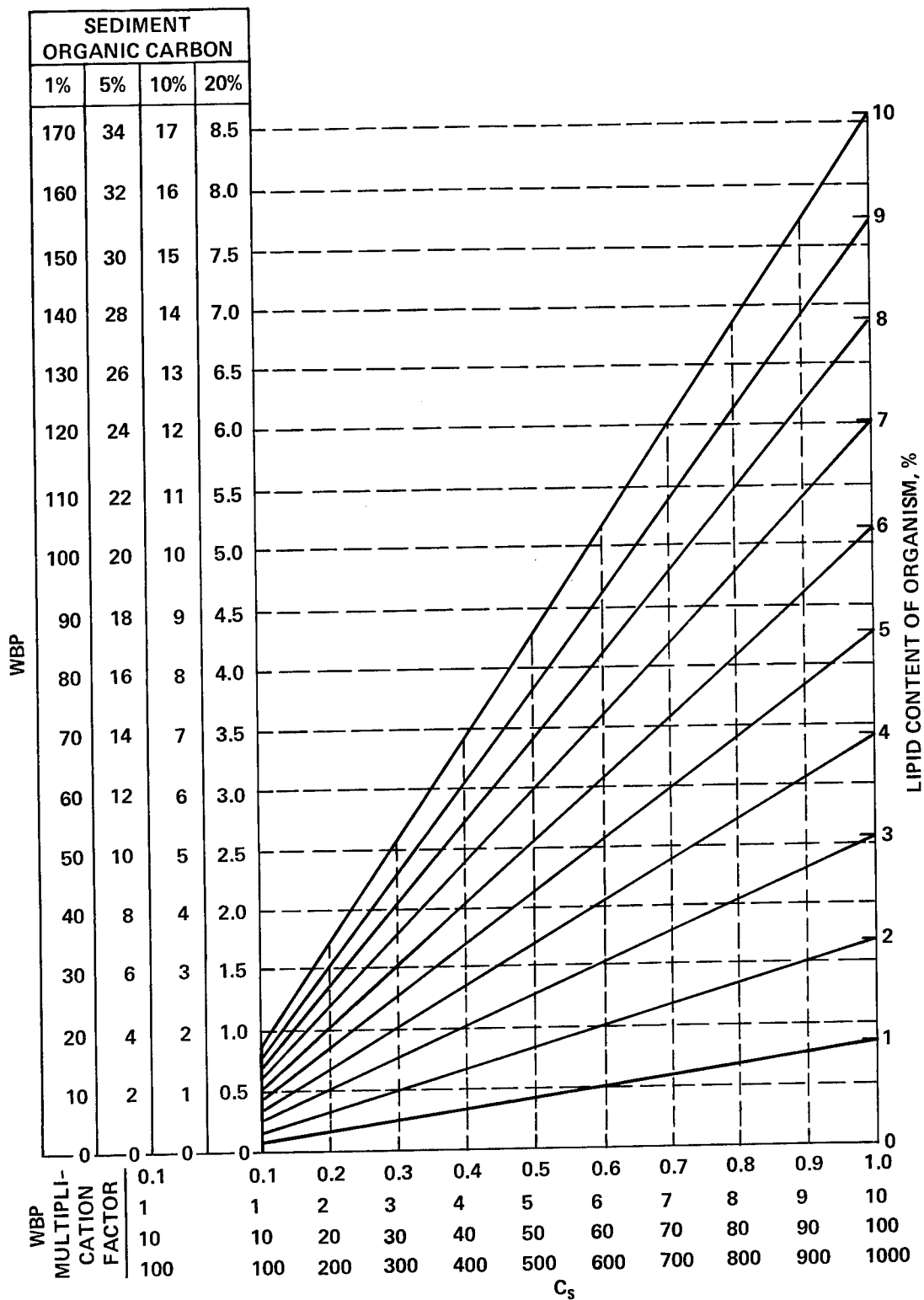


Figure 2. Nomograph for determining bioaccumulation potential (WBP)



STEP 4. From that point, read across to the left-hand vertical axis and select the WBP value from the appropriate sediment organic carbon column expressed as percent of sediment dry weight.

STEP 5. Multiply WBP by the factor (0.1, 1, 10, or 100) corresponding to the selected  $C_s$  range. WBP will then be in the same units of concentration as  $C_s$ .

The lipid scale as well as the  $C_s$  scale of the nomograph can be changed by orders of magnitude by adjusting the WBP scale in the same manner. For example, if the organism of interest is a mussel having 0.3 percent lipid content, one would simply follow the 3-percent lipid line and divide the appropriate resulting WBP value by 10. If the sediment concentration  $C_s$  of a contaminant falls above or below the  $C_s$  ranges shown on the nomograph, then the units of concentration can be changed (e.g., change 0.02 ppm to 20 parts per billion). Interpolation between lipid lines or between organic carbon columns is straightforward because all relationships are proportional. For example, for sediment organic carbon content of 3 percent ( $f_{OC} = 0.03$ ), WBP would be  $1/3$  the WBP value at 1 percent organic carbon,  $5/3$  the WBP value at 5 percent organic carbon,  $10/3$  the WBP value at 10 percent organic carbon, or  $20/3$  the WBP value at 20 percent organic carbon.

To illustrate the use of the nomograph, the regulator may be interested in assessing the potential for bioaccumulation of total PCB by a fish of 5 percent lipid content exposed to the highly contaminated sediment (44 ppm PCB). The regulator would trace the 5-percent lipid line to a  $C_s$  value of 44 and then read across to the 1-percent organic carbon column to obtain a WBP value of about  $38 \times 10$  or 380 ppm. Since the organic carbon content of the sediment is 1.6 percent, a more precise estimate can be made by dividing 380 by 1.6 to obtain a maximum whole-body bioaccumulation potential of 238 ppm. Such a high WBP value might prompt the regulator to impose disposal prohibitions or restrictions without further sediment evaluation. Alternatively, the regulator might decide to conduct Tier II evaluations to project actual PCB bioaccumulation from the highly contaminated sediment by that fish species, as well as to evaluate bioavailability under various disposal options.

The final aspect of the Tier II evaluation in this example, then, is the consideration of bioavailability. Proportion  $p$  of projected bioaccumulation  $C_{ss}$  to bioaccumulation potential WBP for mussels ranged from  $<0.1$  for high

and medium contamination to 0.4 for the reference sediment and 0.8 for low contamination. Since  $p$  is so low for the more highly contaminated sediments, environmental factors that could enhance bioavailability should be considered. Suspension of contaminated sediment in the water column during dredging and disposal operations, for example, would increase the surface area for desorption and could at least transiently increase concentrations of desorbing chemicals available to fish and filter-feeding animals. This is particularly true in freshwater systems. On the other hand, freshwater bivalves often close up when turbidity increases, thus limiting their exposure to contaminants desorbing from suspended particulates.

#### Future Research

Research is being conducted at the WES to define the roles of suspended contaminated sediment, soluble and microparticulate organic carbon, organism life-history strategies, and other environmental variables in determining the bioavailability to aquatic biota of chemicals associated with sediment that must be dredged. From these findings, methods for evaluating the ecological impact of dredging and disposal operations are being developed that will have improved utility and interpretability compared to present methods.

### References

- Blau, G. E., Neely, W. B., and Branson, D. R. 1975. "Ecokinetics: A Study of the Fate and Distribution of Chemicals in Laboratory Ecosystems," *Journal of American Institute of Chemical Engineers*, 21:854-861.
- Geyer, H., Sheehan, P., Kotzias, D., and Korte, F. 1982. "Prediction of Ecological Behavior of Chemicals: Relationship between Physico-chemical Properties and Bioaccumulation of Organic Chemicals in the Mussel *Mytilus edulis*," *Chemosphere*, 11(11):1121-1134.
- Karickhoff, S. 1981. "Semi-empirical Estimation of Sorption of Hydrophobic Pollutants on Natural Sediments and Soils," *Chemosphere*, 10(8):833-846.
- Könemann, H., and van Leeuwen, K. 1980. "Toxicokinetics in Fish: Accumulation and Elimination of Six Chlorobenzenes by Guppies," *Chemosphere*, 9(1):3-19.
- Mackay, D. 1982. "Correlation of Bioconcentration Factors," *Environmental Sciences and Technology*, 16(5):274-278.
- McFarland, V. A. 1984. "Activity-based Evaluation of Potential Bioaccumulation from Sediments," *Dredging '84 Proceedings*, American Society of Civil Engineers, 345 East 47th Street, New York, 1:461-467.
- McFarland, V. A. and Clarke, J. U. 1986, "Testing Bioavailability of Polychlorinated Biphenyls from Sediments Using a Two-level Approach," *Proceedings, USAE Committee on Water Quality, Sixth Seminar*, The Hydrologic Engineering Center, 609 Second Street, Davis, Calif., pp. 220-229.
- SAS Institute Inc. 1985. *SAS User's Guide: Statistics*, Version 5 Edition, Cary, N. C.
- US Environmental Protection Agency/Corps of Engineers Technical Committee on Criteria for Dredged and Fill Material. 1977. "Ecological Evaluation of Proposed Discharge of Dredged Material into Ocean Water; Implementation Manual for Section 103 of Public Law 92-532 (Marine Protection, Research, and Sanctuaries Act of 1972)" (Second printing April 1978), Environmental Effects Laboratory, US Army Engineer Waterways Experiment Station, Vicksburg, Miss.